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(54) PRODUCTION OF THERMOPLASTIC RESIN FOAM

(57)Abstract:

PURPOSE: To obtain a foam of good quality expanded to provide uniform cells by mixing a thermoplastic resin with a specific polytetrafluoroethylene foam stabilizer and a physical foaming agent, extruding and expanding the resultant mixture.

CONSTITUTION: This method for producing a thermoplastic resin foam is to mix (A) 100 pts.wt. thermoplastic resin with (B) 0.01-1.0 pt.wt. polytetrafluoroethylene fine powder as a foam stabilizer, then comprise (C) an organic compound having a lower boiling point than that of the component (A) as a physical foaming agent in the resultant mixture, extrude and expand the prepared mixture. The component (B) has a viscosity so as to flow out ≥1.0g for 10min from a hole having 2.1mm inside diameter and 8.0mm length at 340°C under 20kg/cm2 pressure and its average particle diameter is 5-40μm. Furthermore, the component (B) is uniformly and finely dispersed in the thermoplastic resin without conglomerating therein.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the approach of obtaining the foam to which it was minutely [uniformly] good for and foamed, by being made from thermoplastics.
[0002]
[Description of the Prior Art] The extrusion-foaming method is learned as one of the approaches which obtains thermoplastics foam. An extrusion-foaming method is an approach which thermoplastics is put into an extruder, and fuses, mixes a foaming agent to the fused resin, extrudes resin to a low voltage field from the mouthpiece attached at the tip of an extruder, and makes foam.
[0003] In extrusion foaming, the cellular regulator other than a foaming agent is used. A cellular regulator is also called a foaming nucleating additive, and should serve as a nucleus for generating air bubbles in the case of foaming, and it is thought that it is what also determines the number of the air bubbles generated and the magnitude of air bubbles.
[0004] It has been supposed that various things can be used as a foaming agent for extrusion foaming. If the foaming agent is roughly divided, it will turn into a chemistry foaming agent and a physical foaming agent. It will decompose, if heated, and a chemistry foaming agent generates gas, and is a foaming agent of the type with which the gas which occurred generates air bubbles to resin. On the other hand, a physical foaming agent is a foaming agent of the type which it only evaporates [type] as it is, without causing a chemical reaction when heated, and makes resin generate air bubbles. A chemistry foaming agent is bicarbonate od soda, and it is dinitrosopentamethylenetetramine, and a physical foaming agent is a carbon dioxide and butane.
[0005] Things various also as a physical foaming agent were used. This general classification divides it into an inorganic compound and an organic compound. As an inorganic compound, nitrogen besides the above-mentioned carbon dioxide, water, etc. were used. Moreover, as an organic compound, aliphatic hydrocarbon, halogenated aliphatic hydrocarbon, an alicycle group hydrocarbon, ether, and ketones were used. Aliphatic hydrocarbon is butane and a propane, halogenated aliphatic hydrocarbon is methyl chloride and a dichlorodifluoromethane, alicycle group hydrocarbons are a cyclopentane and a cyclohexane, ether is diethylether, and ketones are acetones.
[0006] Although things various also as a cellular regulator were used, the many were inorganic substance powder. They are a calcium carbonate, talc, a calcium silicate, diatomaceous earth, a barium sulfate, etc. However, organic substance powder was also used as a cellular regulator. For example, the polymer powder of a mono-vinyl aromatic compound was used for making polyethylene foam. In addition, using polytetrafluoroethylene was also known.
[0007] JP,46-19191,B has proposed that a front face makes thermoplastics foam, using the fluorocarbon of a solid-state or a liquid condition as a foaming nucleating additive using an volatile foaming agent, i.e., the physical foaming agent which consists of an organic compound, as a foaming agent. Moreover, it had proposed that JP,2-279739,A also made resin foam using the physical foaming agent which consists of an arrow flare organic compound, using fluorocarbon as a nucleating agent, i.e., a foaming

nucleating additive.

[0008] The fluorocarbon which uses JP,46-19191,B as a foaming nucleating additive presupposes that it is required for a front face to be in a solid-state or a liquid condition, and supposes that things various as an example can be used. For example, it is supposed that you may be the silica covered with perfluoro butanoic acid besides a polytetrafluoroethylene and tetrafluoroethylene-hexafluoropropylene copolymer and solid-state powder like poly hexafluoropropylene, a perfluoro caprylic acid, etc., an alumina, a metal, etc. However, such fluorocarbon was difficult to distribute this in thermoplastics, although there was effectiveness of the formation of detailed [cellular]. That is, there was a fault which fluorocarbon serves as a lump and tends to exist in thermoplastics, therefore produces a big cavity or produces nonuniformity of foaming in foam.

[0009] Moreover, JP,2-279739,A has indicated adding and extruding a hydrocarbon or halogenated hydrocarbon to thermoplastics, foaming to it as halocarbon powder and a foaming agent, as a nucleating agent, at it, and making foam. As an example of halocarbon powder, chlorine or fluorine content powder is mentioned and various polymers besides polytetrafluoroethylene are mentioned. however, having followed instruction of this official report -- if -- as well as instruction of above-mentioned JP,46-19191,B, itis [nodule-] easy toize halocarbon powder in thermoplastics, therefore a big cavity is produced in foam -- ******** -- as a result -- homogeneity -- foam with detailed foaming was not able to be obtained.

[0010]

[Problem(s) to be Solved by the Invention] This invention tends to offer the manufacture approach of foam that the good foam to which the powder added as a cellular regulator distributed uniformly minutely, without nodule-izing in thermoplastics, therefore foamed uniformly minutely is obtained.

[0011]

[Means for Solving the Problem] This artificer mixed various cellular regulators to thermoplastics, foamed by having extruded using various foaming agents including various kinds of fluorocarbon, and observed the cellular condition of the obtained foam. Consequently, when polytetrafluoroethylene special as fluorocarbon was used using the physical foaming agent which consists of an organic compound as a foaming agent, it found out that distributed to homogeneity and air bubbles became uniformly detailed, without fluorocarbon nodule-izing in thermoplastics.

[0012] Polytetrafluoroethylene (henceforth PTF) has been used for Plastic solid manufacture in ancient times. Therefore, PTF marketed so far was for shaping most. Even if this PTF for shaping tends to distribute this in thermoplastics, it has some which exist with a nodule, and it was not able to be distributed uniformly minutely easily. Therefore, when foamed by using the PTF powder for shaping for a cellular regulator, and extruding it, big air bubbles were produced and uniform detailed foam was not able to be obtained.

[0013] However, this artificer mixed this in thermoplastics, presses fit and extrudes the physical foaming agent which becomes this mixture from an organic compound, and made it foam using the powder of special PTF instead of the object for shaping which came to be marketed as an object for lubricants recently as a cellular regulator, and foam was made. Consequently, the obtained foam found out foaming uniformly minutely.

[0014] Moreover, this artificer found out that PTF (this is hereafter called PTF for shaping) generally marketed for Plastic solid manufacture and PTF (this is hereafter called PTF for lubrication) marketed for lubricants could distinguish clearly by those physical properties. One of the physical properties of the is melt viscosity.

[0015] Then, when melt viscosity is explained, for die length, a bore is PTF heated in temperature of 340 degrees C at 2.1mm from the hole it is [hole] 8.0mm 20kg/cm2 When it extrudes for 10 minutes under a pressure, PTF for shaping does not flow out of a hole at all, therefore a melt index is zero. On the other hand, if PTF for lubrication is extruded under the above-mentioned condition, it will flow out of a hole, and the flow of 1.0g or more will be shown, therefore 1.0 or more will be the melt index. Thus, PTF for shaping and PTF for lubrication are clearly distinguishable with melt viscosity.

[0016] Moreover, PTF for shaping differs from PTF for lubrication also in respect of the feel. If the powder of PTF is gathered and adjusted each other between the thumb and a forefinger, the powder of PTF for shaping will serve as a lump, and will become yarn-like, and sensibility like powder that ** also became wet will be given. On the other hand, the powder of PTF for lubrication has given sensibility like the powder which remained with powder without nodule-izing, therefore gathered, did not become yarn-like at all, and got dry exactly, when it **********s between the thumb and a forefinger. Therefore, both can also distinguish a feel top clearly.

[0017] In it including a foaming agent in this, extruding, and making it foam, while this invention mixes a cellular regulator to thermoplastics The physical foaming agent which consists of an organic compound with the boiling point lower than the softening temperature of the above-mentioned thermoplastics as a foaming agent is used. As a cellular regulator with the impalpable powder of PTF The temperature of a hole to 340 degrees C, and 20kg/cm2 whose die length a bore is 8.0mm in 2.1mm It has the viscosity which flows out 1.0g or more in 10 minutes under a pressure. PTF in within the limits whose mean particle diameter is 5-40 micrometers -- using -- the above-mentioned thermoplastics 100 weight section -- receiving -- PTF -- 0.01 - 1.0 weight ******** -- it is related with the manufacture approach of the thermoplastics foam characterized by things.

[0018] The above-mentioned difference between PTF for shaping and PTF for lubrication originates in the difference of the molecular weight of PTF. However, the molecular weight used as the criteria in the case of distinguishing the two does not understand well what kind of value it is. It is said that PTF for lubrication can be made from the phase of carrying out the polymerization of the PTF, by controlling molecular weight. However, since it is fairly difficult, once control of the molecular weight usually makes PTF for shaping of the amount of macromolecules, irradiate a radiation, or heat this to this, it is made to decompose into it, and it cuts a chain, and is making PTF for lubrication. In this case, although a difference is produced in the surface state of resin by whether it is based on a radiation, or it is based on heating, PTF for lubrication then cut with the radiation is suitable for considering as a foaming nucleating additive.

[0019] Moreover, if it says from the structure of resin, PTF for lubrication is suitable for what is porosity using as a cellular regulator. As a porous standard, specific surface area is a thing 1m2 / more than g.

[0020] Although the amount of PTF for lubrication used as a cellular regulator is effective even when it is very little, it is more than the 0.01 weight section to the thermoplastics 100 weight section preferably. Moreover, since only the effectiveness of balancing it does not show up in cellular detailed-ization even if it uses it more than the 1.0 weight sections to the thermoplastics 100 weight section, as for PTF for lubrication, it is desirable to carry out to below the 1.0 weight sections. Moreover, the particle of PTF for lubrication is used as a detailed particle which is in within the limits whose mean particle diameter is 5-40 micrometers. In it, it is still more desirable to be referred to as 10-30 micrometers.

[0021] PTF for lubrication which can be used as a cellular regulator by this invention is marketed. If the resin is shown as grade of a commercial item, with the product by Asahi Glass Co., Ltd., what is sold by the trade name of a "Freon lubricant" can use it as a cellular regulator generally. If that grade is said concretely, the thing of the grade of L169J, L169J-1, XL169 J-A, L150J, L180J, L181J, L171J, and L173J can be used by this invention. The specific surface area is 1-9m2 / g, 5-40 microns and the melting point have in 320-332 degrees C, and bulk density has an average diameter within the limits of 0.34-0.50.

[0022] In this invention, the physical foaming agent which consists of an organic compound with the boiling point lower than the softening temperature of thermoplastics as a foaming agent is used. Although it is desirable to press this fit in the thermoplastics with which melting of the PTF content for lubrication was carried out within an extruder as for the physical foaming agent, before putting into an extruder, it may be included in thermoplastics. The amount of foaming agents is an amount which generally extrudes and is used on the occasion of foaming, and is 1 - 15 weight section to the resin 100 weight section.

[0023] A propane, butane, aliphatic hydrocarbon like a pentane, methyl chloride, halogenated aliphatic hydrocarbon like dichloro difluoroethane, a cyclohexane, an alicycle group hydrocarbon like a cyclopentane, the ketones like an acetone, and ether like diethylether can be used for the physical foaming agent which consists of an organic compound as mentioned above.

[0024] A foaming agent sinks into the thermoplastics with which melting of the PTF content for lubrication was carried out within the extruder as mentioned above, and a fizz constituent is made. This fizz constituent is extruded from the mouthpiece attached at the tip of an extruder to a low voltage field (usually under atmospheric pressure), it foams to the extruded fizz constituent in a low voltage field, and it serves as foam. It is cooled after that and let this foam be a product. These actuation does not have the actuation and the change which extruded until now and have been used in foaming.

[0025] In enforcing this invention approach, the various assistants which extruded until now and have been used in foaming in addition to the above-mentioned ingredient can be used. in using polyethylene terephthalate as thermoplastics, in order [for example,] to improve a melting property -- the [acid 2 anhydride like pyromellitic dianhydride, and / of the periodic table] -- the [1a group or] -- it is independent, or 2a group's metallic compounds, a sodium carbonate, etc. can be mixed and added. Moreover, talc powder little as a foaming nucleating additive can be added, or an antistatic agent, an ultraviolet ray absorbent, etc. can be added.

[0026] As an extruder, it is desirable to use a single screw extruder. What has so far been used for extruding polystyrene, polyethylene, etc. and making them foam can be used for the extruder.

[0027]

[Effect of the Invention] Since a foaming agent is included in this, and it extrudes and is made to foam according to this invention while mixing a cellular regulator to thermoplastics, continuous uniform foam can be manufactured easily. Moreover, since the physical foaming agent which consists of an organic compound with the boiling point lower than the softening temperature of thermoplastics as a foaming agent is used, the foam to which it comparatively often foamed [altitude] can be obtained easily. The impalpable powder of PTF is used as a cellular regulator. Moreover, furthermore, the impalpable powder The temperature of a hole to 340 degrees C, and 20kg/cm2 whose die length a bore is 8.0mm in 2.1mm It has the viscosity which flows out 1.0g or more in 10 minutes under a pressure. Since the cellular regulator of the 0.01 - 1.0 weight section was added to the thermoplastics 100 weight section using the thing in within the limits whose mean particle diameter is 5-40 micrometers The air bubbles of moderate magnitude can generate uniformly minutely by evaporation of a foaming agent within thermoplastics, and an appearance can obtain good and good foam. This effect of the invention is large at this point.

[0028] An example and the example of a comparison are given to below, and the reason which is excellent in this invention approach is clarified concretely. In addition, the section only means the weight section in below. Moreover, although the diameter of average air bubbles of the obtained foam was measured in the following examples and examples of a comparison, the measuring method is ASTM. D It is the approach specified to 2842-69. Moreover, for calling it a melt index below, die length is the powder of the hole whose bore is 8.0mm in 2.1mm as this invention prescribed to PTF at the temperature of 340 degrees C 20kg/cm2 It is a value when expressing the flow when making it flow out in 10 minutes under a pressure with g.

[0029]

[Example 1] Using polystyrene (the Nippon Steel chemistry company make, trade name S CHIREN G-15L) as thermoplastics, as PTF, using Fluon L169J (melt index 6.5g / 10 minutes, mean particle diameter of 13 micrometers) by Asahi Glass Co., Ltd., PTF of the 0.1 sections was added to the polystyrene 100 section, and mixture was made from this example.

[0030] this mixture -- aperture -- a tandem extruder (40mm and 50mm) -- putting in -- an extruder -- on the way -- since -- as a foaming agent -- chlorofluocarbon 142b / methyl chloride -- 50/50% of the weight of mixture -- about 12 % of the weight -- it came out comparatively, pressed fit and extruded in the shape of a rod into atmospheric air from the mouthpiece.

[0031] The consistency was [0.040g / cc / /and the diameter of average air bubbles of the obtained foam] 0.20mm.

[0032]

[Example 2] In the example 1, it carried out like the example 1 except having made PTF into the Asahi Glass Co., Ltd. make and trade name Fluon 169 J-A (a melt index being 6.5g / 10 minutes, and mean particle diameter being 40 micrometers).
[0033] The consistency was 0.04g/cc and the diameter of average air bubbles of the obtained foam was 0.21mm.
[0034]
[Example 3] It carried out like the example 1 except having set PTF to the Asahi Glass Co., Ltd. make and trade name Fluon 171J (a melt index being 2.5g / 10 minutes, and mean particle diameter being 7 micrometers) in the example 1.
[0035] The consistency was 0.04g/cc and the diameter of average air bubbles of the obtained foam was 0.24mm.
[0036]
[The example 1 of a comparison] In the example 1, it carried out like the example 1 except having made PTF into the Asahi Glass Co., Ltd. make and trade name Fluon G163 (a melt index, 10g [0] / minutes, mean particle diameter of 25 micrometers).
[0037] The consistency was 0.04g/cc, the diameter of average air bubbles was 0.30mm, and since air bubbles were big and rough, the obtained foam was not accepted to be good foam.
[0038]
[The example 2 of a comparison] In the example 1, it carried out like the example 1 except having set PTF to the Asahi Glass Co., Ltd. make and trade name Fluon L155J (a melt index, 10 120g / minutes, mean particle diameter of 4 micrometers).
[0039] The consistency was 0.04g/cc, the diameter of average air bubbles was 0.29mm, and since air bubbles were big and rough, the obtained foam was not accepted to be good foam.
[0040]
[Example 4] The mixture of the pyromellitic dianhydride 0.35 section and the sodium-carbonate 0.05 section was made [with the polyethylene terephthalate (Teijin, Ltd. make, trade name TR8580) 100 section] as PTF as thermoplastics, respectively as the Asahi Glass Co., Ltd. make, the trade name Fluon L169J (melt index 6.5g / 10-minute, mean particle diameter of 13 micrometers)0.05 section, and a thickener and a thickening assistant.
[0041] the above-mentioned mixture -- a single screw extruder with an aperture of 65mm -- supplying -- an extruder -- on the way -- since -- as a foaming agent, the 0.9 sections came out comparatively per mixture 100 section, butane was pressed fit, and it was made to extrude and foam into atmospheric air from an in-a-circle extrusion hole
[0042] The consistency was 0.30g/cc, the diameter of average air bubbles was 0.16mm, and the obtained foam had the good appearance. Moreover, the quality of the rate of an open cell of this foam was good at 1.7%.
[0043]
[Example 5] In the example 4, it carried out like the example 4 except having made PTF into the Asahi Glass Co., Ltd. make and trade name Fluon XL169 J-A (a melt index, 10 6.5g / minutes, mean particle diameter of 40 micrometers).
[0044] It was 0.04g/cc, and the consistency of the obtained foam was 0.18mm of diameters of average air bubbles, and its appearance was good.
[0045]
[Example 6] In the example 4, it carried out like the example 4 except having set PTF to the Asahi Glass Co., Ltd. make and trade name Fluon L150J (melt index 120g / 10 minutes, mean particle diameter of 9 micrometers).
[0046] The consistency of the obtained foam was 0.3g/cc, the diameter of average air bubbles was 0.17mm, and the appearance was good foam.
[0047]
[The example 3 of a comparison] an example 4 -- setting -- instead of [of PTF] -- **** for the talc 1.0 weight sections -- it carried out like the example 4 except having considered as things.

[0048] the consistency of the obtained foam -- 0.3g/cc -- it is -- 0.23mm of diameters of average air bubbles -- it is -- air bubbles -- it was big and rough foam. Moreover, the rate of an open cell of this foam was 16%, and was that in which quality is inferior.
[0049]
[The example 4 of a comparison] In the example 4, it carried out like the example 4 except having set PTF to the Asahi Glass Co., Ltd. make and trade name Fluon L155J (melt index 120g / 10 minutes, mean particle diameter of 4 micrometers).
[0050] although the consistency of the obtained foam was 0.3g/cc and it was foam with a good appearance -- the diameter of average air bubbles -- 0.35mm and air bubbles -- it was big and rough foam.
[0051]
[The example 5 of a comparison] In the example 4, it carried out like the example 4 except having made PTF into the Asahi Glass Co., Ltd. make and trade name Fluon G163 (melt index 0g / 10 minutes, mean particle diameter of 25 micrometers).
[0052] the consistency of the obtained foam -- 0.3g/cc -- it is -- 0.20mm of diameters of average air bubbles -- it is -- air bubbles -- it was big and rough foam, and the foam front face had marks where a large number were worn, and was the sheet of a poor appearance.

[Translation done.]